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Process for the telomerization of acyclic olefins

The present invention relates to a process for the telomerization of acyclic olefins having at least two conjugated double bonds (I) with nucleophiles (II) using a metal-carbene complex as catalyst.

For the purposes of the present invention, telomerization is the reaction of olefins having conjugated double bonds (conjugated dienes) in the presence of a nucleophile (telogen). The main products obtained are compounds made up of two equivalents of the diene and one equivalent of the nucleophile.

The products of the telomerization reaction are of industrial importance as versatile precursors for solvents, plasticizers, fine chemicals and intermediates for active compounds. The octadienol, octadienyl ethers or octadienyl esters obtainable from butadiene are potential intermediates in processes for preparing corresponding alkenes.

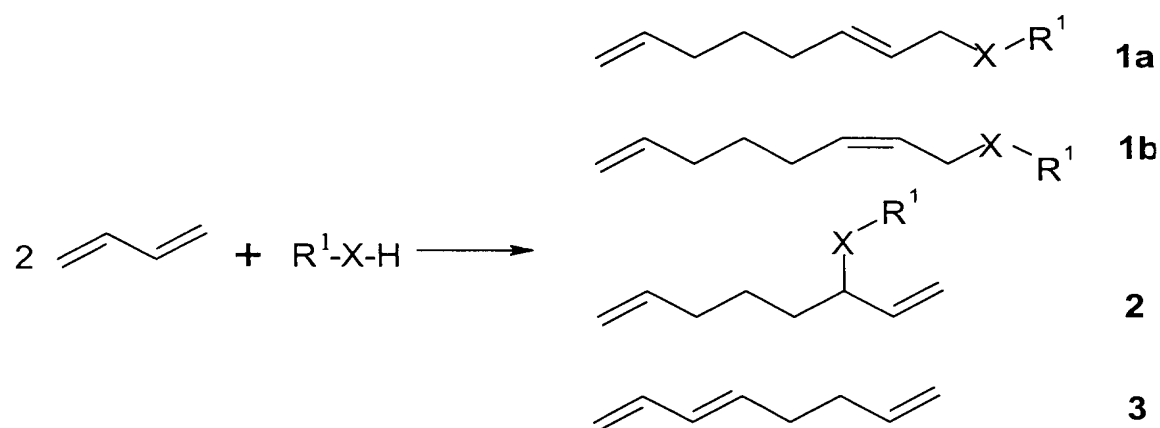
The telomerization of dienes with nucleophiles is an industrially interesting method of adding value to inexpensive, industrially available dienes. Owing to their ready availability, the use of butadiene, isoprene or cracker fractions obtained from these dienes is of particular interest. However, to the present time, the telomerization of butadiene is being employed in practice only by Kuraray in the fine chemicals sector for the synthesis of 1-octanol. The reasons which prevent the wider use of telomerization processes include unsatisfactory catalyst activities, catalyst productivities and selectivity problems with telomerization catalysts. Thus, the known telomerization processes result in high catalyst costs and/or by-products which prevent industrial implementation.

Compounds which have been found to be effective catalysts for telomerization are, inter alia, halogen-free palladium(0) and palladium (II) compounds (A. Behr, in "*Aspects of Homogeneous Catalysis*"; editor R. Ugo, D. Reidel Publishing Company, Doordrecht/Boston/Lancaster, **1984**, Vol. 5, 3). In addition, compounds of other transition metals such as cobalt (R. Baker, A. Onions, R. J. Popplestone, T.N. Smith, *J. Chem. Soc., Perkin Trans. II* **1975**, 1133-1138), rhodium, nickel (R. Baker, D.E. Halliday, T.N. Smith, *J.*

Organomet. Chem. **1972**, 35, C61-C63; R. Baker, *Chem. Rev.* **1973**, 73, 487-530; R. Baker, A.H. Cook, T.N Smith, *J. Chem. Soc., Perkin Trans. II* **1974**, 1517-1524.) and platinum have also been used as catalysts.

- 5 The telomerization of dienes is described comprehensively in the technical literature. In the telomerization of butadiene with methanol, for example, the abovementioned catalysts generally give mixtures of the products **1a**, **1b**, **2**, **3** (below) where $X = O$, $R^a = Me$. Main products are the desired, industrially important linear telomers **1a** and **1b**. However, significant proportions of the branched telomer **2** and of 1,3,7-octatriene **3** are formed.

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- Furthermore, 4-vinyl-1-cyclohexene (Diels-Alder product of butadiene) is formed in variable yields together with, generally in only small amounts, further by-products. This range of products is generally also found when using other nucleophiles having active hydrogen atoms, in which case the corresponding radicals of the respective nucleophile are introduced in place of the methoxy group.

- The significant formation of the abovementioned by-products is a further factor which makes implementation of an economical and environmentally friendly process extraordinarily difficult. Although telomerization of butadiene with methanol has been intensively studied and patented by a number of companies, the abovementioned problems have not been solved satisfactorily.

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In a continuous process described by Dow Chemical in WO 91/09822 in 1989, in which palladium acetylacetonate/triphenylphosphine is used as catalyst, catalyst productivities (turnover numbers) up to 44,000 were achieved. However, the chemoselectivities to the target product **1** at such catalyst turnover numbers are < 85%.

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National Distillers and Chem. Corp. (US 4,642,392, US 4,831,183) described a batch process for the preparation of octadienyl ethers in 1987. Here, the product mixture was separated off from the catalyst (palladium acetate/5 eq. of triphenylphosphine) by distillation, leaving the catalyst as a solution in tetraglyme. The catalyst can be reused up to twelve times, with further phosphine being added each time. However, the first batch gave the linear ether in a yield of only 57% (corresponds to a TON of 2000). The n/iso ratio of product **1** to product **2** is in this case only 3.75:1. In a further patent of National Distillers, the product mixture was separated from the reaction solution by extraction with hexane. The telomerization was carried out in dimethylformamide or sulfolane using the catalyst mixture palladium(II) acetate/3 eq. of triphenylphosphinemonosulfonate. The first batch gave the linear telomer with a TON of 900. The selectivity to the linear alcohol was a low 40%.

Longer-chain primary alcohols such as ethanol, propanol and butanol (J. Beger, H. Reichel, *J. Prakt. Chem.* **1973**, 315, 1067) form the corresponding telomers with butadiene. However, the catalyst activity of the known catalysts is in this case even lower than in the abovementioned cases. Thus, under identical reaction conditions [Pd(acetylacetonate)₂/PPh₃/butadiene/alcohol = 1:2:2000:5000; 60°C/10 h], the telomers of methanol are formed in a yield of 88%, those of propanol are formed in a yield of 65% and those of nonanol are formed in a yield of only 21%.

In summary, it can be said that the known palladium-phosphine catalysts for the telomerization reactions of butadiene with alcohols do not allow satisfactory selectivities of > 95% chemoselectivity and regioselectivity, as required for an ecologically advantageous process, to be achieved.

Like alcohols, carboxylic acids are suitable nucleophiles in telomerization reactions. Acetic acid and butadiene give good yields of the corresponding octadienyl derivatives **1a**, **1b** and **2** with R^a = Me-CO, X = O (DE 2 137 291). The ratio of products **1/2** can be influenced via the

ligands of the palladium (D. Rose, H. Lepper, *J. Organomet. Chem.* **1973**, *49*, 473). A ratio of 4/1 could be achieved using triphenylphosphine as ligand, and the ratio could be increased to 17/1 when tris(o-methylphenyl) phosphite was used. Other carboxylic acids such as pivalic acid, benzoic acid or methacrylic acid and also dicarboxylic acids can likewise be reacted with butadiene.

Shell Oil has described a process based on the telomerization of conjugated dienes with carboxylic acids for the preparation of α -olefins in US 5 030 792.

Telomerization reactions in which water is used as nucleophile have been studied intensively by, inter alia, Kuraray (US 4 334 117, US 4 356 333, US 5 057 631). Here, phosphines, usually water-soluble phosphines, or phosphonium salts (EP 0 296 550) are usually used as ligands. The use of water-soluble diphosphines as ligands is described in WO 98/08 794, and DE 195 23 335 discloses the reaction of alkadienes with water in the presence of phosphonite or phosphinite ligands.

The telomerization of butadiene with nucleophiles such as formaldehyde, aldehydes, ketones, carbon dioxide, sulfur dioxide, sulfinic acids, β -keto esters, β -diketones, malonic esters, α -formyl ketones and silanes has likewise been described.

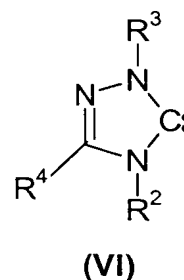
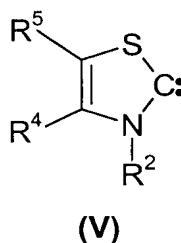
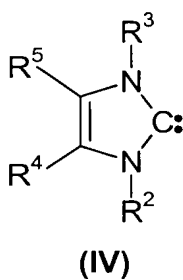
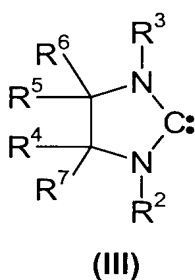
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Most of the work on telomerization has been carried out using butadiene. However, this reaction can also be applied to other dienes having conjugated double bonds. These can formally be regarded as derivatives of butadiene in which hydrogen atoms have been replaced by other groups. Isoprene is of particular industrial importance. Since, in contrast to butadiene, isoprene is an unsymmetrical molecule, telomerization results in formation of further isomers (J. Beger, Ch. Duschek, H. Reichel, *J. Prakt. Chem.* **1973**, *315*, 1077 - 89). The ratio of these isomers is influenced considerably by the type of nucleophile and the choice of ligands.

Owing to the abovementioned importance of the telomerization products and the problems associated with the present state of the art, there is a great need for new catalyst systems for telomerization reactions which make it possible to carry out the reactions on an industrial scale with high catalyst productivity and give telomerization products in high yield and purity.

It has surprisingly been found that the telomerization reactions of an acyclic olefin with a nucleophile are catalyzed by metals of groups 8 - 10 of the Periodic Table and particular carbene ligands so as to give high conversions and selectivities.

- 5 The invention accordingly provides a process for the catalytic telomerization of acyclic olefins having at least two conjugated double bonds (I) with at least one nucleophile (II), wherein complexes comprising metals of groups 8 to 10 of the Periodic Table of the Elements and at least one carbene ligand having one of the formulae



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where

R^2, R^3 :

are identical or different and are each a) a linear, branched, substituted or unsubstituted cyclic or alicyclic alkyl group having from 1 to 24 carbon atoms,

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or b) a substituted or unsubstituted, monocyclic or polycyclic aryl group having from 6 to 24 carbon atoms

or c) a monocyclic or polycyclic, substituted or unsubstituted heterocycle having from 4 to 24 carbon atoms and at least one heteroatom from the group consisting of N, O, S,

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R^4, R^5, R^6, R^7 :

are identical or different and are each

hydrogen, alkyl, aryl, heteroaryl, -CN, -COOH, -COO-alkyl, -COO-aryl, -OCO-alkyl, -OCO-aryl, -OCOO-alkyl, -OCOO-aryl, -CHO, -CO-alkyl, -CO-aryl, -O-alkyl, -O-aryl, -NH₂, -NH(alkyl), -N(alkyl)₂, -NH(aryl), -N(alkyl)₂, -F, -Cl, -Br, -I, -OH, -CF₃, -NO₂, -ferrocenyl, -SO₃H, -PO₃H₂, where the alkyl groups have 1-24 carbon atoms and the aryl groups have

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from 5 to 24 carbon atoms and the radicals R^4 and R^5 may also be part of a bridging aliphatic or aromatic ring,

with the proviso that when the metal of groups 8 - 10 of the Periodic Table is Pd, R^2 and/or R^3 have the meaning c), are used as catalyst.

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R^2 and R^3 are in particular a monocyclic or polycyclic ring which contains at least one heteroatom selected from among the elements nitrogen, oxygen and sulfur and may bear further substituents selected from among the groups -CN, -COOH, COO-alkyl, -COO-aryl, -OCO-alkyl, -OCO-aryl, -OCOO-alkyl, -OCOO-aryl, -CHO, -CO-alkyl, -CO-aryl, -aryl, -alkyl, -O-alkyl, -O-aryl, -NH₂, -NH(alkyl), -N(alkyl)₂, -NH(aryl), -N(alkyl)₂, -F, -Cl, -Br, -I, -OH, -CF₃, -NO₂, -ferrocenyl, -SO₃H, -PO₃H₂. The alkyl groups have from 1 to 24 carbon atoms and the aryl groups have from 5 to 24 carbon atoms. When Pd is used as metal of groups 8 - 10 of the Periodic Table, one or both of the ligands R^2 and R^3 have these meanings.

15 The radicals R^2 , R^3 , R^4 , R^5 , R^6 and/or R^7 can be identical or different and may bear at least one substituent from the group consisting of -H, -CN, -COOH, -COO-alkyl, -COO-aryl, -OCO-alkyl, -OCO-aryl, -OCOO-alkyl, -OCOO-aryl, -CHO, -CO-alkyl, -CO-aryl, -aryl, -alkyl, -alkenyl, -allyl, -O-alkyl, -O-aryl, -NH₂, -NH(alkyl), -N(alkyl)₂, -NH(aryl), -N(alkyl)₂, -F, -Cl, -Br, -I, -OH, -CF₃, -NO₂, -ferrocenyl, -SO₃H, -PO₃H₂, where the alkyl groups have from 1 to 24, preferably from 1 to 20, carbon atoms, the alkenyl groups have from 2 to 24 carbon atoms, the allyl groups have from 3 to 24 carbon atoms and the monocyclic or polycyclic aryl groups have from 5 to 24 carbon atoms.

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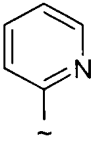
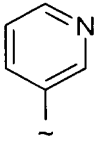
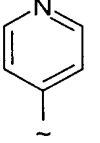
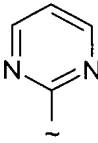
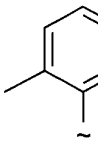
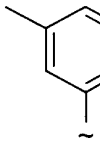
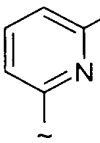
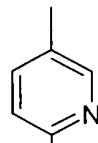
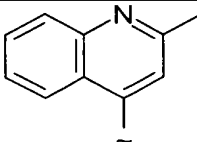
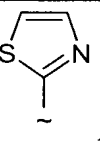
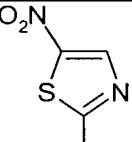
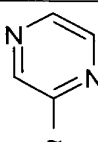
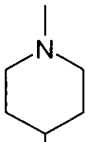
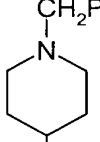
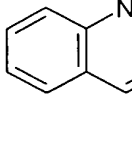
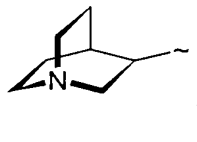
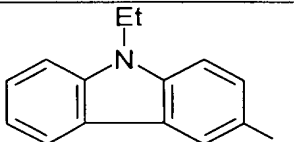
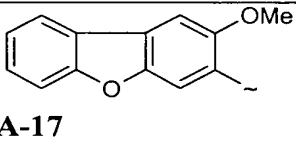
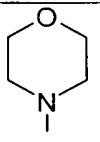
The radicals R_4 to R_6 may also be covalently bound to one another, e.g. via CH₂ or CH groups.

Substituents having acidic hydrogen atoms can also be present as metal or ammonium ions in place of the protons.

The radicals R^2 and R^3 may be, inter alia, monocyclic or polycyclic rings containing at least one heteroatom. These are, for example, radicals which are derived from five- and six-membered heteroalkanes, heteroalkenes and heteroaromatics such as 1,4-dioxane, morpholine, γ -pyran, pyridine, pyrimidine, pyrazine, pyrrole, furan, thiophene, pyrazole, imidazole, thiazole and

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oxazole. Specific examples of such radicals R₂ and R₃ are shown in the table below. In the table below. In the table, ~ in each case indicates the point of linkage to the five-membered heterocycle.

 A-1	 A-2	 A-3	 A-19
 A-4	 A-5	 A-6	 A-7
 A-8	 A-9	 A-10	 A-11
 A-12	 A-13	 A-14	 A-15
 A-16	 A-17	 A-18	

- 5 For the purposes of the present invention, carbene ligands include both free carbenes which can function as ligand and also carbenes coordinated to metals.

Suitable metals can be, for example, Pd, Fe, Ru, Os, Co, Rh, Ir, Ni or Pt.

- 10 In the telomerization carried out by the process of the invention, it is in principle possible to use all acyclic olefins having at least two conjugated double bonds. For the purposes of the

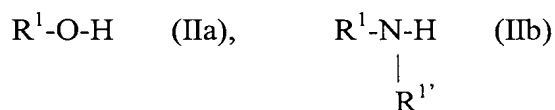
present invention, the use of 1,3-butadiene and isoprene (2-methyl-1,3-butadiene) is preferred. It is possible to use both the pure dienes and mixtures in which these dienes are present.

As mixtures comprising 1,3-butadiene/isoprene, preference is given to using mixtures of 1,3-butadiene or isoprene with other C₃-, C₄- and/or C₅-hydrocarbons. Such mixtures are obtained, for example, in cracking processes for the production of ethene, in which refinery gases, naphtha, gas oil, LPG (liquefied petroleum gas), NGL (natural gas liquid), etc, are reacted. The C₄ fractions obtained as by-product in these processes comprise, depending on the cracking process, variable amounts of 1,3-butadiene. Typical 1,3-butadiene concentrations in the C₄ fraction obtained from a naphtha steam cracker are from 20 - 70% of 1,3-butadiene.

The C₄ components n-butane, i-butane, 1-butene, cis-2-butene, trans-2-butene and i-butene, which are likewise present in these fractions, interfere only inconsequentially, if at all, in the reaction in the telomerization step.

Dienes having cumulated double bonds (1,2-butadiene, allene, etc) and alkynes, in particular vinylacetylene can, on the other hand, act as moderators in the telomerization reaction. It is therefore advantageous to remove the alkynes and possibly the 1,2-butadiene beforehand (e.g. as described in DE 195 23 335). This can, if possible, be carried out by means of physical processes such as distillation or extraction. Possible chemical routes are selective hydrogenation of the alkynes to alkenes or alkanes and reduction of the cumulated dienes to monoenes. Methods of carrying out such hydrogenations are prior art and are described, for example, in WO 98/12160, EP-A-0 273 900, DE-A-37 44 086 or US 4 704 492.

In a preferred embodiment, compounds of the formula (IIa) or (IIb)



where R¹, R^{1'} are identical or different and are each H, a substituted or unsubstituted, linear, branched or cyclic alkyl or alkenyl group having from 1 to 22 carbon atoms, a carboxyl group

or an aryl group and the radicals R^1 , $R^{1'}$ may be joined to one another via covalent bonds, are used as nucleophile (II).

R^1 and $R^{1'}$ may bear identical or different substituents, e.g. one or more substituents selected from the group consisting of -CN, -COOH, -COO-alkyl, -CO-alkyl, -aryl, -alkyl, -COO-Aryl, -CO-aryl, -O-alkyl, -O-CO-alkyl, -N-alkyl₂, -CHO, -SO₃H, -NH₂, -F, -Cl, -OH, -CF₃, -NO₂. The alkyl groups have from 1 to 24 carbon atoms and the aryl groups have from 5 to 24 carbon atoms.

As nucleophiles, preference is given to using any compounds having the formula II. Examples of telogens of the formula II are

- water,
- alcohols and phenols such as methanol, ethanol, n-propanol, isopropanol, allyl alcohol, butanol, octanol, 2-ethylhexanol, isononanol, benzyl alcohol, cyclohexanol, cyclopentanol, 2-methoxyethanol, phenol or 2,7-octadien-1-ol,
- dialcohols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2,3-butanediol and 1,3-butanediol,
- polyols such as glycerol, glucose, sucrose,
- hydroxy compounds such as α -hydroxyacetic esters,
- carboxylic acids such as acetic acid, propanoic acid, butanoic acid, isobutanoic acid, benzoic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 1,2,4-benzenetricarboxylic acid,
- ammonia,
- primary amines such as methylamine, ethylamine, propylamine, butylamine, octylamine, 2,7-octadienylamine, dodecylamine, aniline, ethylenediamine or hexamethylenediamine,
- secondary amines such as dimethylamine, diethylamine, N-methylaniline, bis(2,7-octadienyl)amine, dicyclohexylamine, methylcyclohexylamine, pyrrolidine, piperidine, morpholine, piperazine or hexamethylenimine.

Telogens which can themselves be obtained by a telomerization reaction can be used directly or else be formed in situ. Thus, for example, 2,7-octadien-1-ol can be formed in situ from water

and butadiene in the presence of the telomerization catalyst, 2,7-octadienylamine can be obtained from ammonia and 1,3-butadiene, etc.

Particularly preferred telogens are water, methanol, ethanol, n-butanol, allyl alcohol,
5 2-methoxyethanol, phenol, ethylene glycol, 1,3-propanediol, glycerol, glucose, sucrose, acetic acid, butanoic acid, 1,2-benzenedicarboxylic acid, ammonia, dimethylamine and diethylamine.

The process of the invention is preferably carried out in the presence of a solvent.

10 As solvent, use is generally made of the nucleophile employed, if it is present as a liquid under the reaction conditions. However, it is also possible to use other solvents. The solvents used should be largely inert. Preference is given to the addition of solvents when using nucleophiles which are present as solids under the reaction conditions or in the case of products which would be obtained as solids under the reaction conditions. Suitable solvents include, inter alia,
15 aliphatic, cycloaliphatic and aromatic hydrocarbons such as C₃-C₂₀-alkanes, mixtures of lower alkanes (C₃-C₂₀), cyclohexane, cyclooctane, ethylcyclohexane, alkenes and polyenes, vinylcyclohexene, 1,3,7-octatriene, the C₄-hydrocarbons from C₄ fractions from crackers, benzene, toluene and xylene; polar solvents such as tertiary and secondary alcohols, amides such as acetamide, dimethylacetamide and dimethylformamide, nitriles such as acetonitrile and
20 benzonitrile, ketones such as acetone, methyl isobutyl ketone and diethyl ketone; carboxylic esters such as ethyl acetate, ethers such as dipropyl ether, diethyl ether, dimethyl ether, methyl octyl ether, 3-methoxyoctane, dioxane, tetrahydrofuran, anisole, alkyl and aryl ethers of ethylene glycol, diethylene glycol and polyethylene glycol and other polar solvents such as sulfolane, dimethyl sulfoxide, ethylene carbonate, propylene carbonate and water. Ionic liquids,
25 for example imidazolium or pyridinium salts, can also be used as solvents.

The solvents are used either alone or as mixtures of various solvents or nucleophiles.

The temperature at which the telomerization reaction is carried out is in the range from 10 to
30 180°C, preferably from 30 to 120°C, particularly preferably from 40 to 100°C. The reaction pressure is from 1 to 300 bar, preferably from 1 to 120 bar, particularly preferably from 1 to 64 bar and very particularly preferably from 1 to 20 bar.

In the process of the invention, it is essential that the telomerization reaction is carried out using catalysts based on metal complexes having carbene ligands of the formulae III to VI.

- 5 Examples of carbene ligands corresponding to the formulae III to VI and complexes in which such ligands are present have been described in the technical literature (W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2257; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162; W.A. Herrmann, T. Weskamp, V.P.W. Böhm, *Advances in Organometallic Chemistry*, **2001**, *Vol. 48*, 1-69; D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39-91).

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However, only few examples of carbene ligands and complexes bearing heterocyclic substituents are known (J.C.C. Chen, I.J.B. Lin, *Organometallics* **2000**, *19*, 5113).

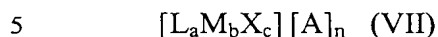
The catalyst metal of groups 8 to 10 of the Periodic Table can be introduced into the process in
15 various ways:

- a) as metal-carbene complexes,
- b) in the form of precursors from which the catalysts are formed in situ.

Option a)

- 20 Metal-carbene complexes have been described in the technical literature (cf. W. A. Herrmann, C. Köcher, *Angew. Chem.* 1997, 109, 2257; *Angew. Chem. Int. Ed. Engl.* 1997, 36, 2162; W.A. Herrmann, T. Weskamp, V.P.W. Böhm, *Advances in Organometallic Chemistry*, 2001, Vol. 48, 1-69; D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* 2000, 100, 39-91; J.C.C. Chen, I.J.B. Lin, *Organometallics* 2000, 19, 5113) and are obtainable by various
25 routes. For example, the complexes can be formed by addition of carbene ligand onto metal compounds. This can be achieved with expansion of the ligand sphere or by breaking up of bridge structures. Metal compounds of the formula I can often be obtained from simple compounds of metals of groups 8 to 10 of the Periodic Table, e.g. salts or metal complexes (acetates, acetylacetonates, carbonyls, etc) by reaction with the carbene ligands. A further
30 possibility is the replacement of ligands coordinated to the central metal by the carbene ligands. In this case, less strongly coordinating ligands (e.g. solvent molecules) are displaced by the carbene ligands.

For the purposes of the present invention, preference is given to using metal-carbene complexes having the formula



where

M is a metal of groups 8 to 10 of the Periodic Table of the Elements, X is a charged or uncharged, monodentate or polydentate ligands bound to the metal atom and

10 A is a singly charged anion or the chemical equivalent of a multiply charged anion, b is an integer from 1 to 3, a is an integer from 1 to $4 \times b$, c = 0 or an integer from 1 to $4 \times b$ and n = 0 or an integer from 1 to 6.

The group A is preferably a halide, sulfate, phosphate, nitrate, pseudohalide, tetraphenylborate, 15 tetrafluoroborate, hexafluorophosphate or carboxylate ion, among the latter preferably the acetate ion, or else a metal complex anion, for example tetrachloropalladate, tetrachloroaluminate, tetrachloroferrate(II), hexafluoroferrate(III), tetracarbonylcobaltate.

The monodentate or polydentate ligands which may be present in the complexes of Fe, Ru, Co, 20 Rh, Ir, Ni, Pd and Pt in addition to the carbene ligands are shown in the formula (VII) as X. X is hydrogen or the hydrogen ion, a halogen or halogen ion, pseudohalide, carboxylate ion, sulfonate ion, amide group, alkoxide group, acetylacetonate group, carbon monoxide, alkyl radical having from 1 to 7 carbon atoms, aryl radical having from 6 to 24 carbon atoms, isonitrile, nitrogen ligand, (for example nitrogen monoxide, nitrile, amine, pyridine), 25 monoolefin, diolefin, alkyne, allyl group, cyclopentadienyl group, π -aromatic or phosphorus ligand which coordinates via the phosphorous atom. Phosphorus ligands are preferably compounds of trivalent phosphorus, e.g. phosphines, phosphites, phosphonites, phosphinites. If a plurality of ligands X are present in the metal complex, they can be identical or different.

30 If the substituents of the carbene ligands of the formulae III to VI bear functional groups, these can likewise coordinate to the metal atom (chelating coordination, also described as hemilabile coordination in the literature (J.C.C. Chen, I.J.B. Lin, Organometallics 2000, 19, 5113).

Option b)

The metal carbene complexes are formed in situ from precursors and carbene ligand or a carbene ligand precursor.

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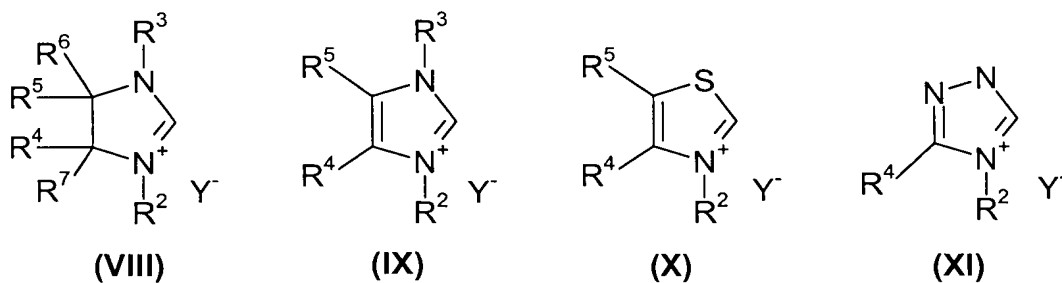
As precursors of the metal complexes of groups 8 - 10 of the Periodic Table, it is possible to use, for example, salts or simple complexes of the metals, for example metal halides, metal acetates, metal acetylacetonates, metal carbonyls.

- 10 For the purposes of illustration, some specific examples of palladium compounds are palladium(II) acetate, palladium(II) chloride, palladium(II) bromide, lithium tetrachloropalladate, palladium(II) acetylacetonate, palladium(0)-dibenzylideneacetone complexes, palladium(II) propionate, bis(acetonitrile)palladium(II) chloride, bis(triphenylphosphine)-palladium(II) dichloride, bis(benzonitrile)palladium(II) chloride, bis(tri-*o*-tolylphosphine)-
 15 palladium(0). Analogous compounds of the other metals of groups 8 to 10 of the Periodic Table can likewise be used.

The carbenes of the formulae III to VI are used in the form of free carbenes or as metal complexes or are generated in situ from carbene precursors.

20

Suitable carbene precursors are, for example, salts of the carbenes having the formulae VIII to XI,



25

where R², R³, R⁴, R⁵, R⁶, R⁷ are as defined above and Y is a singly charged anionic group or, corresponding to the stoichiometry, part of a multiply charged anionic group.

Examples of Y are halides, hydrogensulfate, sulfate, phosphate, alkoxide, phenoxide, alkylsulfates, arylsulfates, borates, hydrogen carbonate, carbonate, alkylcarboxylates, arylcarbonates.

5

The carbenes can be liberated from the corresponding salts of the carbenes, if appropriate by reaction with an additional base. Suitable bases are, for example, metal hydrides, metal alkoxides, carbonylmetalates, metal carboxylates, metal amides or metal hydroxides.

- 10 The concentration of the catalyst, formally reported in ppm (mass) of catalyst metal based on the total mass, is from 0.01 ppm to 1000 ppm, preferably from 0.5 to 100 ppm, particularly preferably from 1 to 50 ppm.

- 15 The ratio [mol/mol] of carbene to metal is from 0.01:1 to 250:1, preferably from 1:1 to 100:1, particularly preferably from 1:1 to 50:1. In addition to the carbene ligands, further ligands, for example phosphorus ligands such as triphenylphosphine, may be present in the reaction mixture.

- 20 Owing to the catalyst activities and stabilities, it is possible to use extremely small amounts of catalyst in the process of the invention. Apart from a procedure in which the catalyst is reused, there is also the option of not recycling the catalyst. Both variants have already been described in the patent literature (WO 90/13531, US 5 254 782, US 4 642 392).

- 25 It is often advantageous to carry out the telomerization reaction in the presence of bases. Preference is given to using basic components having a pK_b of less than 7, in particular compounds selected from the group consisting of amines, alkoxides, phenoxides, alkalimetal salts and alkaline earth metal salts.

- 30 Suitable basic components are, for example, amines such as trialkylamines which may be alicyclic or/and open-chain, amides, alkali metal salts or/and alkaline earth metal salts of aliphatic or/and aromatic carboxylic acids, e.g. acetates, propionates, benzoates, or corresponding carbonates, hydrogencarbonates, alkoxides of alkali metals and/or alkaline earth

metals, phosphates, hydrogenphosphates or/and hydroxides, preferably of lithium, sodium, potassium, calcium, magnesium, cesium, ammonium and phosphonium compounds. Preferred additives are hydroxides of alkali metals and alkaline earth metals and metal salts of the nucleophile of the formula II.

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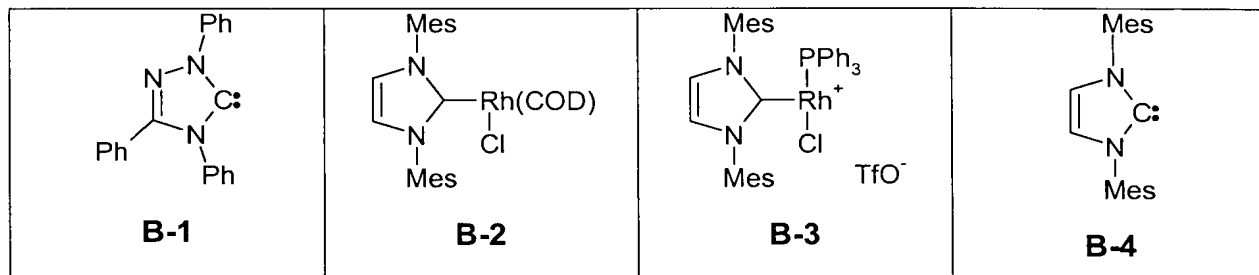
In general, the basic component is used in an amount of from 0.01 mol% and 10 mol% (based on the olefin), preferably from 0.1 mol% to 5 mol% and very particularly preferably from 0.2 mol% to 1 mol%.

- 10 In the process of the invention, the ratio [mol/mol] of diene used to nucleophile used is from 1:100 to 100:1, preferably from 1:50 to 10:1, particularly preferably from 1:10 to 2:1.

The process of the invention can be carried out continuously or batchwise and is not restricted to the use of particular types of reactor. Examples of reactors in which the reaction can be
15 carried out are stirred tank reactors, cascades of stirred vessels, flow tubes and loop reactors. Combinations of various reactors are also possible, for example a stirred tank reactor connected to a downstream flow tube.

- The following examples illustrate the invention without restricting the scope of the patent
20 application.

Examples



Mes = mesityl (2,4,6-trimethylphenyl); COD = 1,5-cyclooctadiene; the bonding of the heterocyclic carbene ligand to the metal is, as in the technical literature, shown in the form of a single bond rather than as a double bond; TfO⁻ = trifluoromethanesulfonate

5

Example 1 – Telomerization of 1,3-butadiene with methanol

211 g of degassed methanol, 589 g of 1,3-butadiene, 1.20 g of sodium hydroxide, 50 g of cyclooctane (internal GC standard) and 0.50 g of 4-t-butylcatechol were placed in a 3 liter autoclave (from Büchi) under protective gas and heated to 80°C. 0.0494 g of palladium acetylacetonate and 0.1078 g of the compound 5-methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazoline (from which the carbene **B-1** can be formed by elimination of methanol) were separately dissolved in 48.4 g of degassed methanol under protective gas. The reaction was started by introducing the solution (from a pressure burette) into the autoclave and the course of the reaction was monitored by gas-chromatographic analysis of samples taken at regular intervals. After 180 minutes, 18% of the butadiene had reacted, and the selectivity of the reaction to 2,7-octadien-1-yl methyl ether was > 96.8% according to gas-chromatographic analysis.

Example 2

Synthesis of the complex **B-2**: 60 mg of [Rh(COD)Cl]₂ (M = 493.08 g/mol) are dissolved in 2 ml of THF (tetrahydrofuran) and admixed at room temperature with 76 mg of the carbene **B-4** (M = 304.3 g/mol) dissolved in 1 ml of THF while stirring. The solution is stirred for 3 hours, the THF is removed under reduced pressure, the precipitate is dissolved in CH₂Cl₂ and filtered. The CH₂Cl₂ is removed under reduced pressure, the residue is washed with pentane, filtered off and dried under reduced pressure. The yield is 82% (110 mg, M = 550.97 g/mol).

25

Example 3

Synthesis of the complex **B-3**: 113.6 mg of **B-2** (0.21 mmol, M = 550.97 g/mol), dissolved in 5 ml of THF are admixed at RT with 53 mg of AgOTf (0.01 mmol, M = 256.94 g/mol) and 57 mg of PPh₃ (0.21 mmol, M = 262.28 g/mol) dissolved in 10 ml of THF. The AgCl which precipitates is filtered off and the THF is removed under reduced pressure. The residue is taken up in CH₂Cl₂, filtered and part of the CH₂Cl₂ is removed under reduced pressure. The complex is precipitated from a little CH₂Cl₂ by addition of pentane, filtered off, washed with pentane and dried under reduced pressure. The yield is 171.8 mg, 90 % (M = 926.88 g/mol).

10 Examples 4 and 5**General method for the telomerization of butadiene with methanol:**

In a 100 ml Schlenk tube, the appropriate amount of catalyst is dissolved in 16.1 g of methanol under protective gas. The solution is admixed with 1 mol% (based on the amount of 1,3-butadiene used) of sodium methoxide (base) and 5 ml of isooctane (internal GC standard).

- 15 The reaction solution is subsequently drawn into the evacuated autoclave (100 ml autoclave from Parr), the autoclave is cooled to T < -10°C and 13.6 g of 1,3-butadiene are condensed in (amount determined by loss in mass of the butadiene stock bottle). The autoclave is warmed to the reaction temperature and then cooled to room temperature after 16 hours. Unreacted 1,3-butadiene is condensed back into a cold trap cooled by means of dry ice. The reaction mixture in the reactor is analyzed by gas chromatography.

The telomerization of 1,3-butadiene with methanol was carried out in accordance with the general method using the complexes B-2 and B-3. The reaction temperature was 90°C.

- 25 The main product obtained in the reaction was 1-methoxyocta-2,7-diene (n product). In addition, 3-methoxyocta-1,7-diene (iso product), 1,3,7-octatriene (OT), 1,7-octadiene (OD) and vinylcyclohexene (VCEN) were formed.

Ex. No.	MeOH : butadiene	Cat.	Rh [Mol-%]	Base [Mol-%]	n+iso [%]	n :iso [%]	OT+OD+VC H [%]	TON
4	1:2	B-2	0.021	1	4.6	97.7:2.3	2.4	219
5	1:2	B-3	0.021	1	1.1	95:5	2.7	52

n + iso = Yield of n product and iso product

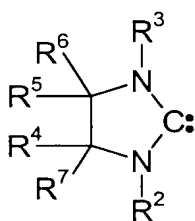
n : iso = Ratio of n product to iso product

OT+OD+VCH = Yield of 1,3,7-octatriene, 1,7-octadiene, vinylcyclohexene (total)

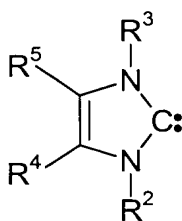
TON = turnover number

Claims:

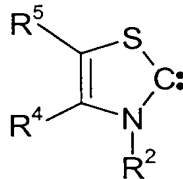
1. A process for the catalytic telomerization of acyclic olefins having at least two conjugated double bonds (I) with at least one nucleophile (II),
 5 wherein complexes comprising metals of groups 8 to 10 of the Periodic Table of the Elements and at least one carbene ligand having one of the formulae



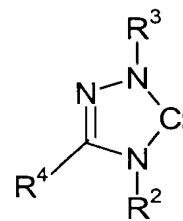
(III)



(IV)



(V)



(VI)

where

- 10 R^2, R^3 : are identical or different and are each a) a linear, branched, substituted or unsubstituted cyclic or alicyclic alkyl group having from 1 to 24 carbon atoms,
 or b) a substituted or unsubstituted, monocyclic or polycyclic aryl group having from 6 to 24 carbon atoms
 15 or c) a monocyclic or polycyclic, substituted or unsubstituted heterocycle having from 4 to 24 carbon atoms and at least one heteroatom from the group consisting of N, O, S,

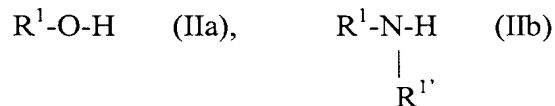
R^4, R^5, R^6, R^7 : are identical or different and are each

- 20 hydrogen, alkyl, aryl, heteroaryl, -CN, -COOH, -COO-alkyl, -COO-aryl, -OCO-alkyl, -OCO-aryl, -OCOO-alkyl, -OCOO-aryl, -CHO, -CO-alkyl, -CO-aryl, -O-alkyl, -O-aryl, -NH₂, -NH(alkyl), -N(alkyl)₂, -NH(aryl), -N(alkyl)₂, -F, -Cl, -Br, -I, -OH, -CF₃, -NO₂, -ferrocenyl, -SO₃H, -PO₃H₂,
 25 where the alkyl groups have 1-24 carbon atoms and the aryl groups have from 5 to 24 carbon atoms and the radicals R^4 and R^5 may also be part of a bridging aliphatic or aromatic ring,

with the proviso that when the metal of groups 8 - 10 of the Periodic Table is Pd, R² and/or R³ have the meaning c), are used as catalyst.

2. The process as claimed in claim 1, wherein R², R³, R⁴, R⁵, R⁶ and R⁷ are identical or different and have at least one substituent from the group consisting of -H, -CN, -COOH, -COO-alkyl, -COO-aryl, -OCO-alkyl, -OCO-aryl, -OCOO-alkyl, -OCOO-aryl, -CHO, -CO-alkyl, -CO-aryl, -aryl, -alkyl, -alkenyl, -allyl, -O-alkyl, -O-aryl, -NH₂, -NH(alkyl), -N(alkyl)₂, -NH(aryl), -N(alkyl)₂, -F, -Cl, -Br, -I, -OH, -CF₃, -NO₂, -ferrocenyl, -SO₃H, -PO₃H₂, where the alkyl groups have from 1 to 24, the alkenyl groups have from 2 to 24 carbon atoms, the allyl groups have from 3 to 24 carbon atoms and the aryl groups have from 5 to 24 carbon atoms.

3. The process as claimed in claims 1 or 2, wherein compounds of the formula (IIa) or (IIb)



where R¹, R^{1'} are identical or different and are each H, a substituted or unsubstituted, linear, branched or cyclic alkyl or alkenyl group having from 1 to 22 carbon atoms, a carboxyl group or an aryl group and the radicals R¹, R^{1'} may be joined to one another via covalent bonds, are used as nucleophile (II).

4. The process as claimed in claim 1 or 2, wherein water, alcohols, phenols, polyols, carboxylic acids, ammonia and/or primary or secondary amines are used as nucleophile (II).
5. The process as claimed in any of claims 1 to 4, wherein 1,3-butadiene or isoprene is used as acyclic olefin (I).
6. The process as claimed in any of claims 1 to 5, wherein 1,3-butadiene in admixture with other C₃-, C₄- and/or C₅-hydrocarbons is used as acyclic olefin (I).

7. The process as claimed in any of claims 1 to 6 carried out in a solvent, where the nucleophile (II) and/or inert organic solvents is/are used as solvent.
- 5 8. The process as claimed in any of claims 1 to 7, wherein the ratio of carbene ligand to metal [mol/mol] is from 0.01:1 to 250:1.

Abstract

- 5 The invention relates to a process for the telomerization of acyclic olefins having at least two conjugated double bonds (I) or mixtures in which such olefins are present with nucleophiles (II) using a metal-carbene complex as catalyst.